

## \* NOTICES \*

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## CLAIMS

(37)(Claim(2))

- (Claim 1)  
 (A) An organic polymer which has a hydroxyl group or a hydrolytic basis combined with a silicon atom, and has at least one carbon-carbon bond which has a bridge for forming a siloxane bond,  
 (B) One or more carbon-carbon bonds which have a carboxylic acid titanium, carboxylic acid potassium, carboxylic acid barium, carboxylic acid manganese, a hardenability constituent containing one or more sorts of carboxylic acid metal salt chosen from carboxylic acid nickel,  
 (Claim 2)  
 (C) The hardenability constituent according to claim 1 which becomes considering an amine compound as an essential ingredient as an ingredient.

- (Claim 3)  
 (A) A number average molecular weight is within the limits of 500-50,000, and an organic polymer of an ingredient is a general formula to an end and/or a side chain of a main chain (1):



the inside of a formula, R<sup>1</sup> and R<sup>2</sup> — respectively — independent — the alkyl group of the carbon numbers 1-20, it is the Tori ORGANO alloy group shown by the aryl group of the carbon numbers 9-20, the aralkyl group of the carbon numbers 7-20, or (R<sup>2</sup>) SiO— (R<sup>2</sup> is the substitution or the unsubstituted hydrocarbon group of the carbon numbers 1-20 independently, respectively). X is a hydroxyl group or a hydrolytic basis independently, respectively, a is 0, 1, 2, or 3, b is 0, 1, or 2, and a and b are not simultaneously set to 0, m is an integer of 0, or 1-19.  
 The hardenability constituent according to claim 1 or 2 coming out and having one or more hydrolytic silyl groups per molecule expressed.

(Claim 4)

The hardenability constituent according to claim 3, wherein X is an alkoxy group.

(Claim 5)

(A) A hardenability constituent given in any 1 paragraph of Claims 1-4 whose organic polymers of an ingredient are a polyoxallylene series polymer and/or a saturated hydrocarbon system polymer.

(Claim 6)

The hardenability constituent according to claim 5 which is a polymer, wherein said saturated hydrocarbon system polymer has a repeating unit resulting from isobutylene 50% of the weight or more in a total amount.

(Claim 7)

(B) Carboxylic acid calcium of an ingredient, carboxylic acid vanadium, carboxylic acid titanium, A hardenability constituent given in any 1 paragraph of Claims 1-8 to which carboxylic acid potassium, carboxylic acid barium, carboxylic acid manganese, and carboxylic acid nickel use as the main ingredients carboxylic acid metal salt expressed with general formula (2), (3), and (6) — (10).

respectively,

Ca(OOCR)<sub>2</sub> (2)

V(OOCR)<sub>3</sub> (3)

Ti(OOCR)<sub>4</sub> (6)

K(OOCR)<sub>4</sub> (7)

Ba(OOCR)<sub>2</sub> (8)

Mn(OOCR)<sub>2</sub> (9)

nickel(OOCR)<sub>2</sub> (10)

(The inside R of a formula is substitution or an unsubstituted hydrocarbon group, and may include a carbon carbon double bond.)

(Claim 8)

(B) The hardenability constituent according to any one of claims 1 to 7 whose carboxylic acid metal salt of an ingredient is the carboxylic acid metal salt in which the melting point has an acid radical of carboxylic acid which is 65 °\* or less.

(Claim 9)

(B) The hardenability constituent according to any one of claims 1 to 7 which is the carboxylic acid metal salt, which has an acid radical of carboxylic acid whose carbon numbers in which carboxylic acid metal of an ingredient contains carbon of a carboxyl group are 2-17.

(Claim 10)

(B) A hardenability constituent given in any 1 paragraph of Claims 1-8 which are metal salt of a carboxylic acid group contained compound in which carboxylic acid metal salt of an ingredient is chosen from octyloic acid, 2-ethylhexanoic acid, neo decanoic acid, oleic acid, or naphthenic acid.

(Claim 11)

(A) A hardenability constituent given in any 1 paragraph of Claims 1-10 containing the (B) ingredient of quantity which serves as 0.005 - 5 weight section by metallic element conversion contained in the (B) ingredient to ingredient: 100 weight section.

(Claim 12)

(A) A hardenability constituent given in any 1 paragraph of Claims 2-10 containing the (B) ingredient of quantity which serves as 0.005 - 5 weight section by metallic element conversion contained in the (B) ingredient, the (C) ingredient 0.01 - 20 weight sections to ingredient: 100 weight section.

[Translation done.]

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## DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]

In this invention, it has the hydroxyl group or hydrolytic basis combined with the silicon atom, and a siloxane bond is formed. Therefore, it is related with the hardenability constituent containing the organic polymer which has a silicon content group (hereinafter a "reactive silicon group") which can construct a bridge.

[0002]

[Description of the Prior Art]

It is known that the organic polymer which contains at least one reactive silicon group in a molecule has the feature that the polymer which constructs a bridge by formation of the siloxane bond is obtained by the hydrolytic reaction of a reactive silicon group, etc., and a rubber-like hardened material is obtained with hygroscopic surface moisture etc. also in a room temperature.

[0003]

In the polymer which it has, these reactive silicon groups a polyoxymethylene series polymer and a polyisobutylene system polymer. It is indicated by JP.552-73988.A, JP.H5-125272.A, JP.H3-75527.A, JP.S63-6003.A, JP.S63-6041.A, JP.H1-38407.A, JP.H6-231758.A, etc.

Especially a polyoxymethylene series polymer and a polyisobutylene system polymer are already produced industrially, and are widely used for uses, such as a sealing material, adhesives, and a paint.

[0004]

When an organic polymer is a saturated hydrocarbon system polymer especially, since it excels in heat resistance, a water resisting property, weatherability, etc., if the hardened material obtained is used for a structural sealing material, the sealing material for multiple glass, etc., it is effective. The isobutylene system polymer which has a repeating unit which furthermore originates in isobutylene 80% of the weight or more in a total amount is preferred as a sealant aiming at moisture proof from especially the thing to excel in low moisture permeability and low gas permeability.

[0005]

Such a sealing material generally fills up the joined part and cures between various members, the sticky nature to the part ranging from being used to a long period of time in order to give a well-cured and an adhesion becomes very important, and revealing sufficient elongation and intensity is required for.

[0006]

Amine compounds, such as diaryl amine, are used together as a co-catalyst in many cases for the purpose of a silanol condensation catalyst being used for bridge construction and accelerating a polymer which, on the other hand, has such a reactive silicon group, and also accelerating a condensation reaction. As such a silanol condensation catalyst, divalent tin, such as octylo acid (2-ethylhexanoic acid) tin. The tin series catalyst represented by trivalent tin, such as dibutyltin bisacetate/lactonate, is used widely, and when the movement of the part which places especially a sealing material is large, since the hardened material which has stability is obtained, many divalent tin is used.

[0007]

However, when octylo acid tin which is divalent tin, for example, is used together with the amine compound of a co-catalyst and is used as a curing catalyst of the (A) ingredient, the intensity and elongation of a hardened material which are acquired may be insufficient, and an improvement of the further physical properties is desired.

[0008]

Although most is a dibutyltin type, the latter trivalent tin series catalyst being used now. While the hardened material obtained has emulsion, i.e., having the character to follow to the long-term stress change from the outside and fast curability, it is broadly used from the ability to apply as a curing catalyst of a liquid molding nature constituent. However, since today only a small amount of octylo acid tin is contained in the composition, it is questionable, development of the silanol condensation catalyst of a non-tin series is desired.

[0009]

In JP.S35-7955.B, JP.S32-3742.B, JP.S35-9639.B, JP.S37-3271.B, etc. As a curing catalyst of an organopolysiloxane constituent, the carboxylic acid metal salt of various kinds of non-tin is indicated with carboxylate of tin. As an example in which the carboxylic acid metal salt of non-tin was used for the curing catalyst of the constituent which, on the other hand, contains the organic polymer which has a reactive silicon group. Although there were carboxylic acid lithium (JP.H5-39428.A, JP.H6-12880.A) and carboxylic acid cerium (JP.2000-313814.A), there was no example broadly examined in various carboxylic acid metal salt until now.

[0010]

Problem(s) to be Solved by the Invention]

The purpose of this invention is as follows.

Have practical hardenability and stability with a good hardened material obtained.

Provide a hardenability constituent useful as the structural sealing material asked especially for high durability, the sealing material for multiple glass, the moisture seal material used for an electronic electronic component, adhesives, etc. from revealing the outstanding intensity and elongation.

[0011]

[Means for Solving the Problem]

In order that this invention persons may solve such a problem, as a result of inquiring, as a curing catalyst of the (A) ingredient Carboxylic acid calcium, Carboxylic acid vanadium, carboxylic acid iron, carboxylic acid titanium, carboxylic acid potassium, By using one or more sorts of carboxylic acid metal salt chosen from carboxylic acid barium, carboxylic acid manganese, carboxylic acid nickel, carboxylic acid cobalt, and a carboxylic acid zirconium. Securing moderate hardenability and stability, it finds out revealing high intensity and the physical properties of high elongation compared with a case where octylo acid tin is used as a curing catalyst, and came to complete this invention.

[0012]

Namely, this invention has a hydroxyl group of a hydrolytic basis combined with the (A) silicon atom. An organic polymer which has at least one silicon content group which can construct a bridge by forming a siloxane bond, (B) it is related with a hardenability constituent containing one or more sorts of carboxylic acid metal salt chosen from carboxylic acid calcium, carboxylic acid vanadium, carboxylic acid titanium, carboxylic acid potassium, carboxylic acid barium, carboxylic acid manganese, and carboxylic acid nickel.

[0013]

An amine compound is related with the aforementioned hardenability constituent which becomes as an essential ingredient as a (C) ingredient.

[0014]

As a desirable embodiment, a number average molecular weight is within the limits of 500-90,000, and as a silicon polymer of the (A) ingredient is a general formula to an end and/or a side chain of a main chain (1):

[0015]

[Formula 2]











cetyl group, a stearyl group, a behenyl group, etc. — usually — 10-30 — a long-chain alkyl group of 10-20 is raised preferably. Like a case of R<sup>7</sup>, an alkyl group of R<sup>8</sup> may be independent and may be mixed two or more sorts.

Although a chain of this vinyl system copolymer consists of a monomeric unit of a formula (18) and a formula (19) substantially, a "real target" here means that the sum total of a monomeric unit of a formula (18) which exists in this copolymer, and a formula (19) surpasses 50 % of the weight. The sum total of a monomeric unit of a formula (18) and a formula (19) is 70 % of the weight or more preferably.

From a point of compatibility with a polyoxyalkylene series polymer, as for an abundance ratio of a monomeric unit of a formula (18), and a monomeric unit of a formula (19), 95:5-40:60 are preferred at a weight ratio, and 90:10-60:40 are still more preferred.

A number of units other than a formula (18) which may be contained in this copolymer, and a formula (19). For example, carboxylic acid groups, such as acrylic acid and methacrylic acid, acrylamide, amide groups, such as methacrylamide, N-methylmethacrylamide, and N-acryloylmaleimide. Enzyme groups, such as glycidyl acrylate and glycidyl methacrylate. Diethylenimine ethyl acrylate, diethylenimine vinyl methacrylates. A monomer containing amino groups, such as aminomethyl vinyl ether, a monomeric unit which originates in acrylonitrile, styrene, alpha-methylstyrene, alkyl vinyl ether, VCM/PVC, vinyl acetate, vinyl propionate, ethylene, etc. in addition to the units exposed.

Although an organic polymer which blends a saturated hydrocarbon system polymer which has a reactive silicon group, and a vinyl-base polymer which has a reactive silicon group is indicated by JP H1-168764 A, JP 2000-186176 A, etc., it is not limited to in particular these.

[0093] A method of polymerizing an acrylic ester (meta) system monomer elsewhere under existence of an organic polymer which has a reactive silicon group as a manufacturing method of an organic polymer which blends a vinyl-base polymer which has a reactive silicon group can be used. Although this manufacturing method is concretely indicated by each gazette, such as JP 59-78223A, JP 59-168014A, JP 60-228516A, and JP 60-228517A, it is not limited to these.

[0094] Carboxylic acid calcium used as a (B) ingredient is a hardenability constituent of this invention. Carboxylic acid vanadium, carboxylic acid iron, carboxylic acid titanium, carboxylic acid potassium, One or more sorts of carboxylic acid metal salt chosen from carboxylic acid barium, carboxylic acid manganese, carboxylic acid nickel, carboxylic acid cobalt, and a carboxylic acid zirconium, it functions as what is called a aligned condensation catalyst in which a siloxane bond may be made to form from a hydroxyl group combined with a silicon atom contained in an organic polymer which is the (A) ingredient of this invention, or a hydroxyl basis.

In said carboxylic acid metal salt, carboxylic acid calcium, carboxylic acid vanadium, Carboxylic acid iron, carboxylic acid titanium, carboxylic acid potassium, carboxylic acid barium, carboxylic acid manganese, and a carboxylic acid zirconium. It is more desirable from a point that the activity of a catalyst is high, carboxylic acid calcium, carboxylic acid vanadium, carboxylic acid iron, carboxylic acid titanium, and a carboxylic acid zirconium are still more preferred, and carboxylic acid iron and carboxylic acid titanium are especially the most preferred.

[0098] Carboxylic acid calcium, carboxylic acid vanadium, carboxylic acid titanium, carboxylic acid potassium, carboxylic acid barium, carboxylic acid manganese, carboxylic acid nickel, carboxylic acid cobalt, and a carboxylic acid zirconium. It is more desirable from a point with little coloring of a hardenable constituent obtained, and a point that the heat resistance of a hardened material and weatherability which are obtained are high, and carboxylic acid calcium, carboxylic acid titanium, carboxylic acid potassium, carboxylic acid barium, and a carboxylic acid zirconium are still more preferred.

[0097]

formula (2) – (12), respectively.

liquid state and carboxylic acid metal salt which has the acid radical becomes a thing which has a solid state or viscosity and it is hard to deal with it (workability = bad). On the contrary, when a carbon number of said carboxylic acid is small (e.g., molecular weight is small), catalytic ability of carboxylic acid metal salt may fall [carboxylic acid metal salt which has the acid radical] including mostly an ingredient which volatilizes easily with heating. Especially on conditions (thin layer) which extended a constituent think, volatilization by/heating may be large and catalytic ability of carboxylic acid metal salt may fall greatly. Therefore, as for the group of carboxylic acid metal salts, it is more preferred that it is 3-13, and it is more preferred that it is especially 5-10.

Especially acquisition is easy, and is cheap and a point that compatibility with the (A) ingredient is good to said carboxylic acid has 2-ethylhexanoic acid, octylic acid, neo decanoic acid, oleic acid, or preferred naphthoic acid. Said naphthoic acid is expressed with an empirical formula (20).



carboxylic acid (2-ethylhexanoic acid etc.) whose carbon atoms in which said carboxylic acid adjoins a carbon atom which adjoins a quaternary carbon (neo decanoic acid) which is a carbonyl group are the third class carbon and carboxylic acid (n-octanoic acid) which is a quaternary carbon A pivalic acid, are more preferred from a cure rate being quick, and especially carboxylic acid whose carbon atom which adjoins a carbonyl group is quaternary carbon is preferred.

[0102] From a viewpoint of availability and compatibility, as an example of desirable carboxylic acid metal salt, 2-ethoxybenzoic acid iron (divalent), 2-ethoxybenzoic acid iron (trivalent), 2-ethoxybenzoic acid sodium (trivalent), 2-ethoxybenzoic acid vanadium (trivalent), 2-ethoxybenzoic acid calcium (trivalent), 2-ethoxybenzoic acid potassium (univalent), 2-ethoxybenzoic acid barium (divalent), 2-ethoxybenzoic acid manganese (divalent), 2-ethoxybenzoic acid titanium (trivalent), 2-ethoxybenzoic acid cobalt (divalent), 2-ethoxybenzoic acid zirconium (trivalent), 2-ethoxybenzoic acid nickel (divalent), 2-ethoxybenzoic acid neodecanoic acid iron (trivalent), neo decanoic acid iron (divalent), neo decanoic acid vanadium (trivalent), neo decanoic acid calcium (divalent), neo decanoic acid potassium (univalent), Neo decanoic acid sodium (divalent), neo decanoic acid zirconium (trivalent), Oleic acid iron (trivalent), oleic acid iron (divalent), oleic acid titanium (trivalent), Oleic acid vanadium (trivalent), oleic acid iron (trivalent), oleic acid potassium (univalent), oleic acid barium (divalent), manganese oleate (divalent), oleic acid nickel (divalent), oleic acid cobalt (divalent), An oleic acid zirconium (trivalent), naphthenic acid iron (divalent), naphthenic acid titanium (trivalent), naphthenic acid calcium (divalent), naphthenic acid sodium (divalent), naphthenic acid potassium (univalent), naphthenic acid vanadium (trivalent), calcium naphthenate (divalent), titanium (trivalent), naphthenic acid barium (divalent), manganese naphthenate (divalent), naphthenic acid nickel (divalent), cobalt naphthenate (divalent), a naphthenic acid zirconium (trivalent), naphthenic acid, etc. are mentioned.

[illegible]

[0194] From a viewpoint of coloring to yellow, 2-ethylhexanoic acid titanium (tetraavalence), 2-ethylhexanoic acid calcium (divalent), 2-ethylhexanoic acid potassium (univalent), 2-ethylhexanoic acid barium (divalent), 2-ethylhexanoic acid sodium (univalent), 2-ethylhexanoic acid magnesium (divalent), 2-ethylhexanoic acid zinc (divalent), 2-ethylhexanoic acid strontium (divalent), 2-ethylhexanoic acid cerium (divalent), neo decanoic acid titanium (tetraavalence), neo decanoic acid calcium (divalent), neo decanoic acid potassium (univalent), neo decanoic acid barium (divalent), neo decanoic acid sodium (univalent), neo decanoic acid magnesium (divalent), neo decanoic acid zinc (divalent), oleic acid titanium (tetraavalence), oleic acid calcium (divalent), oleic acid potassium (univalent), oleic acid barium (divalent), oleic acid sodium (univalent), oleic acid magnesium (divalent), oleic acid zinc (divalent), naphthenic acid titanium (tetraavalence), calcium naphthenate (divalent), zirconium naphthenate (univalent), naphthenic acid barium (divalent), and a naphthenic acid zirconium (tetraavalence) are more preferred.

[0105]

Such carboxylic acid metal salt makes a carboxylic acid group content compound, or its ester and sodium hydroxide react, and makes solution of hard soap. Solution of metal salt prepared apart from this in addition, a sedimentation method which settles metallic soap. A carboxylic acid group content compound or its ester and metal hydroxide, an oxide, a method etc. to react in [dis.], such as chlorides, and a carboxylic acid group content compound are made to react in [dis.], such as saponification to which a weak acid salt is made to react in an elevated temperature, and direct method to which a carboxylic acid group content compound and metal powder are made to react, [an anhydrous organic solvent are taken

As for such carboxylic acid metal salt, it is preferred to dilute with diluting solvents, such as a mineral spirit, toluene, hexylene glycol, a paraffin oil, and dioctyl phthalate, and to be used with a solvent whose metal content is about 1 to 40 % of the weight.

(B) About 0.005–5 weight sections are prepared at metallic element conversion contained in the (B) ingredient to (A) ingredient 100 weight section as amount of ingredient used, and also about 0.01–3 weight sections are prepared. (B) Since a cure rate may become slow and a hardening reaction will become fully obtained if loadings of an ingredient are less than this range, it is not desirable. On the other hand, if loadings of an ingredient are more than this range, the hardening reaction will become expedient, but become a material will become expansion of heat and forming local of this time of hardening arise, and as hard to be obtained, if loadings of the (B) ingredient exceed this range.

[0108] The aforementioned carboxylic acid calcium, carboxylic acid vanadium, carboxylic acid iron, carboxylic acid titanium, carboxylic acid potassium, carboxylic acid barium, carboxylic acid sodium, carboxylic acid lithium, carboxylic acid cobalt, and a carboxylic acid zinc compound. Besides using it alone, it can be used combining two or more sorts, also can use together with carboxylic acid tin salt, carboxylic acid lead salt, carboxylic acid bismuth salt, carboxylic acid ceric salt, etc.

[illegible]

In this invention, an amino group content silane coupling agent can also be used as a (C) ingredient. Said amino group content silane coupling agent is a compound which has a basis (phenothiazine, hydroxy silicon group) and an amino group containing a silicon atom which a hydrophobic basis combined. As an example of this hydrophobic amino group, X mention a basis thing which is a hydrophobic basis among bases comprised with a general formula (1). Although a basis already illustrated as a basis, it is not specifically mentioned, a methoxy group, an ethoxy basis, etc. are preferred as a basis of a hydrophobic basis. As for especially the two or more number of a hydrophobic basis,



As a hardening agent of an epoxy resin, a publicly known hardening agent for epoxy resin can be used widely conventionally. For example, triethylenetetramine, tetraethylenepentamine, diethylenetriamine, N-aminophenyl piperazine, m-xylene diamine, m-phenylenediamine, Diaminodiphenylmethane, diaminodiphenyl sulfone, isophorondiamine, Amine, such as 2,4,6-tris(dimethylamino)phenyl phenol, Tertiary amine salts, polyamide resin, and acrylamide. In addition, various hardening agents such as enamines, imide derivatives, and cyclohexanone. Boron trifluoride complex compounds, phthalic anhydride, hexahydro phthalic anhydride, Anhydrous carboxylic acid, such as tetrahydro phthalic anhydride and methylene tetrahydro phthalic anhydride, a DODESHENR succinic anhydride, pyromellitic anhydride, and anhydrous KURUREN acid, azobisisobutyronitrile, and carboxylic acid can be mentioned.

[0125] An epoxy resin receives reactive-silicon-group containing organic-polymer 100 weight section. It is preferred to use it in the range of one to 100 weight section and also ten to 50 weight section, and it is preferred to blend a hardening agent of an epoxy resin per epoxy resin 100 weight section in the range of one to 200 weight section and also ten to 100 weight section.

[0126] An ingredient which limitation in particular does not have in the method of preparation of a hardenability constituent of this invention, for example, was described above is blended. It kneads under ordinary temperature or heating using a mixer, a roll, a kneader, etc. or an ingredient is dissolved using a little suitable solvents, and a usual method of mixing may be adopted. A 1 liquid type, two-component type, or many liquid type compound can also be built and used by combining these ingredients suitably.

[0127] If a hardenability constituent of this invention is exposed into the atmosphere, by operation of moisture, it will form network structure in three dimensions, and will harden it to a solid which has rubber-like elasticity.

[0128] In a hardenability constituent of this invention, various additive agents can be added if needed. Other during catalysts as an example of solid active for example, metal compounds (elemental tin, stannous chloride, etc.), Adhesive grant agents which improve the adhesive characteristics of a hardened material to glass, ceramic, substrate, metal, rubber, and a flame coupling agent. An antioxidant, radical inhibitors, ultraviolet ray absorber, a metal deoxidizer, anti-ozonant, light stabilizer, the Lynn system peroxide decomposition agent, lubricant, paints, a foaming agent, a photo-setting resin, a rheotropic grant agent, etc. are raised.

[0129] An example of such an additive is indicated in each gazette of JP-4-490555-B, JP-7-106928-B, JP-63-254149-A, and JP-64-22304-A, for example.

[0130] Since a hardenability constituent of this invention has outstanding weatherability, heat resistance, water resisting property, and electric insulation resulting from a principal chain skeleton and it has high intensity and a physical-properties improvement effect of high elongation. It can use conveniently for electrical insulation materials, such as electric electronic component materials, such as a structural elastic sealing compound, a sealing material for multiple glass, a solar cell rear-face sealing agent, pre-insulation an electric wire material for cables, a binder, adhesives, a paint infusion, a coating material, a sealing agent for rust prevention / water proof, etc. It is especially useful when used for adhesives, a structural elastic sealing compound, or a sealing material for solder.

[0131] [Example] Although working example and a comparative example explain this invention concretely below, this invention is not limited to this.

(A) As a working example, a polyurethane system polymer (Kansai Corp. make, trade name EP055SSisobutylene system polymer / aarufin) process all is 100/50 150 weight section which has a reactive silicon group as an ingredient. Epoxy resin (product [made from Oil recovery Shell Epoxy], trade name Epicatec 828) 5 weight section, Hydrogenation alpha-olefin oligomer (product [made from

Idemitsu Petrochemistry], trade name PAC900A) 60 weight section, Colloid calcium carbonate (Maruo Calcium Co., Ltd. make, trade name SHRETTUSU 50 50 weight section, Colloid calcium carbonate (Maruo Calcium Co., Ltd. make, trade name MC-50 50 weight section, Heavy-calcium carbonate (product [made from Shirohata Calcium], trade name SOUTON 3200) 40 weight section, Photo-setting resin (Toagosei make, trade name AKONIKUSU M-300) 3 weight section, Benzotriazole system ultraviolet ray absorbent (Sasagawa Chemicals Co., Ltd. make, trade name SANORU LS-770) 1 weight section, Hindered phenolic antioxidant (Chiba-Ogata Chemicals Co., Ltd. make, trade name IRUGA NOX 1010) 1 weight section, and water 5 weight section were measured respectively, and it often kneaded with a 3 point roll, and was considered as base resin.

[0132] next — as the (B) ingredient: — octyloic acid (2-ethylhexanoic acid) calcium salt (the Nihon Kagaku Sangyo Co., Ltd. make), The trade name NIKKANAFU Chicks Ca 5% toluene solution was used as a hardening agent Lin / for the thing for which distasteful amine (the Kao Corp. make, Firm D18) is respectively shown in Table 1 as a (C) ingredient and which could number / of weight sections / — measure, could use the spatula, and was stirred and mixed / working example 1 ]

[0133] here — as the (B) ingredient of this invention — naphthenic acid vanadium (the Nihon Kagaku Sangyo Co., Ltd. make), as a trade name NIKKANAFU textile V 2% toluene solution and the (C) ingredient — distasteful amine (the Kao Corp. make), The number of weight sections ]—used thing which shows Firm D18 in Table 1 respectively is made into working example 2, (B) as an ingredient — octyloic acid (2-ethylhexanoic acid) iron (the Nihon Kagaku Sangyo Co., Ltd. make), The number of weight sections ]—used thing which shows respectively lauryl amine (made by Wako Pure Chemical Industries, Ltd.) in Table 1 as a trade name NIKKANAFU Chicks Fe 5% toluene solid and the (B) ingredient — octyloic acid (2-ethylhexanoic acid) titanium (the Nihon Kagaku Sangyo Co., Ltd. make), The number of weight sections ]—used thing which shows respectively lauryl amine (made by Wako Pure Chemical Industries, Ltd.) in Table 1 as a trade name NIKKANAFU Chicks Ti 5% toluene solid and the (B) ingredient — octyloic acid (2-ethylhexanoic acid) titanium (the Nihon Kagaku Sangyo Co., Ltd. make), The number of weight sections ]—used thing which shows lauryl amine in Table 1 respectively as (B) octyloic acid (2-ethylhexanoic acid) in (Japanese east transformation Make, trade name neo SUTAN U-20) and a (C) ingredient was made into the comparative example 1.

[0134] These base resin and hardening agents were mixed by the ratio shown in Table 1, respectively, and what constructed the aluminum base material to H type in accordance with the manufacturing method of the tensile adhesive property specimen to which this is specified JISA5758-1992 was filled up. Care-of-health conditions were made into 23 ±x37 ±x50 seven days. [ per day ] The used aluminum uses the alumina treatment aluminum of the 905050-mm size based on JIS H4000 as a substrate, After purifying by methyl ethyl ketone (made by Wako Pure Chemical Industries, Ltd.) before being filled up with the compound, the primer (the Tokyo Industries Dow Corning make, trade name D-2) was dried and used under ordinary temperature for spreading and 30 minutes.

[0135] In accordance with the tensile cement test method of 5758 — 1952 N of JIS A, the examination was presented with H type sample obtained by the above-mentioned method in condition of speed of— testing 30 mm/min under 23 ±° and the climatostat chamber of 50±5% of humidity.

[0136] The recovery was measured by the following methods. First, after making H type sample which ended the above-mentioned care of health immersed into 50 ±° warm water for one day and taking it out, it was neglected under the room temperature on the 1st. Subsequently, after having compressed and fixed to 70% so that sample thickness might be set to 12 to 8.4 mm, and heating a sample in 100 ±° hot air drying equipment for one day, it released from compression and was neglected under the room temperature on the 1st. The thickness of the sample in this case was measured and the recovery to a compressed part was computed.

[0137] Time (tearover-covered time) until it fills the same compound in an obtinent can simultaneously as a measure which estimates hardenability and stretches a hide on the surface under 23 ±° and the



plate. On each substrate which purified the surface by methyl ethyl ketone, 1 liquid mold-curing nature constituent was placed from 1 liquid cartridge using commercial cancer to the crest shape with a 1 cm [in width] × length of about 3 cm, and it was recuperated for 23 ± 14-150 days per day. The manual friction test was done after care of health, cutting an adhesion side deeply with a cutter knife, and the surface of the substrate was observed. The filled hardened material is that cohesive failure is shown, and CF in Table 2 is a fracture state searched for as a sealing material.

[0142]

Depths hardenability took out the portion which has hardened the surface which filled in the 80-mm-long polyethylene tube 1 liquid mold-curing nature constituent produced in working example 5, and was made at the tip of a tube in it at 16.5 mm in inside diameter on the day which the days to measure visited, and measured the hardened thickness with slide calipers.

[0143]

In order to check the practicality as a 1 liquid mold-curing nature constituent, where 1 liquid cartridge filled up with a constant amount, it was used for two weeks in the hot air drying equipment which circulates the temperature control to 50 ± 4, and the depths hardenability after storage was investigated.

[0144]

A result is shown in Table 2.

[0145]

[Table 2]

配合表	成分		実施例6		比較例2	
	(A)成分	製品名				
	可塑剤	PPG3000	95	95	重量部	
	炭酸カルシウム	白炭素CCR	120	120	重量部	
	光安定剤	サノールLS-770	1	1	重量部	
	紫外線吸収剤	チズピン327	1	1	重量部	
	クレー防止剤	デュシバロン#6500	2	2	重量部	
	酸化チタン	タイベークR-820	20	20	重量部	
	脱水剤	A-171	2	2	重量部	
	接着性付与剤	A-1120	3	3	重量部	
	(B)成分	オクテリル銀ジメチルニウム U-220	6.1		重量部	
	(C)成分	ラウリルアルミン	1.4	2	重量部	
H型引張機械特性		M50	0.27	0.19	MPa	
		M100	0.38	0.31	MPa	
		M150	0.46	0.40	MPa	
		TB(断面強度)	0.84	0.93	MPa	
接着性		EB(経断伸び)	520	570	%	
		陽極酸化アルミニウム 塩化銅板	CF	CF	破壊状態 破壊状態	
硬化性	深部硬化性	23°C×1週間	7.7	10.6	mm	
		23°C×2週間	12.2	15.6	mm	
貯蔵安定性 (50°C×2週間貯蔵)	深部硬化性	23°C×1週間	7.2	10.6	mm	
		23°C×2週間	12.0	16.4	mm	

As opposed to the polyether system polymer which serves as the (A) ingredient of this invention in working example 5, (B) By using the lauryl amine which acts the carboxylic acid zirconium salt which acts as a co-catalyst as a (C) ingredient further as a silanol condensation catalyst as an ingredient, Although hardenability was slightly inferior as compared with the comparative example 2, the obtained ductility (ductility) acetone was almost equal to that of the comparative example 2, and the elongation and an adhesion property were excellent, and it checked that 1 liquid mold-curing nature constituent which has sufficient practical use was obtained (Table 2). (Synthetic example 1)

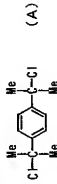
Use polypropylene prior of the molecular weight 3,000 [about 1] as an initiator, and propylene oxide is polymerized in a zinc hexa cyanocobaltate glyme complex compound catalyst. Number average molecular weight about 25,000 (polystyrene reduced molecular weight in which the column measured the solvent using THF using the TOSOH TSK-GEL H type using TOSOH HLC-8120GPC as a liquid-

standing system) polypropylene oxide was obtained. Then, the methanol solution of NaOMe of the equivalent was added 1.2 times to the hydroxyl group of this hydroxyl group and polypropylene oxide, and methanol was distilled off, and also the allyl chloride was added, and the hydroxyl group of the monomer was changed into the allyl group. By the above, the end obtained 3 organic-functions polypropylene oxide of the number average molecular weight 26,000 [about 10<sup>4</sup>] which is an allyl group. [1046]

The nitrogen purge was carried out, after having added 500 g of allyl and 3 organo-functions. The polypropylene oxide and 10 g of hexane which were obtained above to 1L autoclave, deshydrating azeotropically at 90 °C and distilling off hexane under decompression. On the other hand, after adding 30mmol of platinum divinyl disiloxane complex (it is 3% of the weight of xylene solution by platinum complex) 1.0 g of dimethoxymethylsilane was dropped. After making the mixed solution reset at 20 °C for 2 hours, unreacted dimethoxymethylsilane was distilled off under decompression and the residue silicon group content polyoxalkylene series polymer (A-1) was obtained. The number average molecular weight of the obtained polyoxalkylene series polymer (A-1) was about 25,000. The allyl group introduction rate was measured by the following methods by  $^1\text{H-NMR}$  (it measures in a  $\text{CDCl}_3$  solvent using JEOL JNM-LA400). Relative-value of the peak integral value of the allyl and proton (near the  $\text{CH}_2\text{-CH-CH}_2$ -3.1 ppm) to the peak integral value of the  $\text{CH}_3$  group (near 1.2 ppm) of the polypropylene oxide main chain of said allyl and 3 organo-functions polypropylene oxide before a hydrosilylation reaction. Relative value of the peak integral value of the  $\text{CH}_3$  group (near 1.2 ppm) of the polypropylene oxide main chain of the allyl and polypropylene oxide (A-1) after a hydrosilylation reaction. The relative value of the peak integral value of the proton (near  $\text{CH}_2\text{O-CH}_2$ -4.6 ppm) of the methylene group combined with the silicon atom of the end allyl group. Two  $\frac{\text{**}}{\text{**}}$  al, allyl group introduction rate (% $\times 2$ ) (% $\times 1$ ) was 78%.

(Synthetic example 2)

After attaching a three-way cock to the resisting pressure glass container of 2L and carrying out the nitrogen purge of the inside of a container to 1 using an injector, in a container 262.5 ml of nitrocyhexane (thing dy neglecting 1 or more night with the molecular sieves 3A), and 787.5 ml of toluene (thing dy neglecting 1 or more night with the molecular sieves 3A), p-DOC (the following compound (A)) 4.85g (11 mmole) was added.



Next, the melting pressure glass purified gas extraction pipe with a needle valve containing 438 ml (5.15 mmol) of isobutylene monomers was connected to the three-way cock, and after attaching the polymerization vessel all over dry  $\text{N}_2$ /ethanol bath of  $-70^\circ\text{C}$  and cooling, the inside of a container polymerization vessel using the vacuum pump. After opening the needle valve and introducing an isobutylene monomer in a polymerization vessel from a purified gas extraction pipe, the inside of a container was returned to ordinary pressure by introducing nitrogen from one side in a three-way cock. Next, 0.72 g (17 mmol) of 2-methylpyridine was added. Next, 10.58 ml (96.5 mmol) of titanium tetrachloride was added, and the polymerization was started. 70 minutes after the polymerization start, 7.20 g (63.0 mmol) of allyl trimethylsilane was added, and the introduction reaction of the allyl group was continued to molecular chain terminals. After adding allyl trimethylsilane and 200 ml of water, washed [120 minutes], the reaction solution 4 times, the allyl and isobutylene system polymer was obtained by distilling off a solvent.

[0148]

Subsequently, the allyl and isobutylene system polymer 200g obtained in this way, the paraffin-base

name Diana process PS-32 100g and carrying out temperature up to about 75 °C, the  $7.5 \times 10^{-6}$  equivalent was added [methyl dimethoxysilane] for 2.4 Eq and a platinum (vinyl siloxane) complex to the allyl group of an end to the allyl group of an end, and the hydrosilylation reaction was performed. FT-IR (Shimadzu IR-408) performed reaction pursuit, and the absorption based on the olefin of 1640  $\text{cm}^{-1}$  disappeared in about 20 hours.

[0149]

A 2/1 of PS-32 which is the isobutylene styrene polymer and plasticizer group have a reactive silicon atom in both ends of the target chain of the mixtures (A-2) of the weight ratio were obtained.

[0150]

In this way, if the obtained polymer is measured by the GPC method (it was considered as the liquid-injection method), and for the solvent the column used CHCl<sub>3</sub> using Shodex K-804 using LOMODEL made from Waters). The number average molecular weight was 17,600 and Mw/Mn (ratio of weight ending with water). The number average molecular weight was 123. <sup>1</sup>H-NMR (using the Varian Gemini300). The proton which belongs to each structure by measurement in CDCl<sub>3</sub> (the proton average molecular weight to a number average weight) was 123. <sup>1</sup>H-NMR (using the Varian Gemini300). The proton which belongs to each structure by measurement in CDCl<sub>3</sub> (the proton of initiator group: 6.5–7.5 ppm). The methyl proton combined with the silicon atom of polymer-terminal origin. As a result of measuring and measuring the intensity of 0.0–0.1 ppm and the resonance signal of methoxy protons 3.4 – 3.5, the end silyl functional group number Fm (number of the silyl group per one molecule of isobutylene polymer) was 1.76.

(Working example 8–15, comparative example 3)

(A) As an ingredient, various additive agents were measured, respectively, and it often kneaded with a 3 paint roll according to the formula shown in Table 2, using the reactive silicon group content polyoxysilylene series polymer (A-1) obtained in the synthetic example 1, and was considered as base resin.

[01517]

Next, as the (B) ingredient which is a dilute condensation catalyst, luryl amine was further measured for the various carboxylic acid metal salt shown in Table 1 to the above-mentioned resin as is (C) ingredient, the spatula was used for it, and it stirred and mixed for 3 minutes. It was made for all the numbers of mols of the metal atom containing the number of addition parts of the various carboxylic acid metal salt of the (B) ingredient to become the same. The mold about 3 mm thick was used and filled up with the spatula after mixing and care of health on 23  $\pm$  0.5  $\pm$  0.5 deg the 4th was performed. [Per day] from the obtained hardened material sheet, the 3 type (A) and (B) metal salt specimen specified to JIS K 5300 was obtained. The specimen was placed in the ultraviolet microscope (M50) in the time of fixing extended 50%, the intensity at the time of fixation was measured, and the dull fracture (Tb) and the elongation at the time of a dumbbell fracture (Eb) were then measured.

[0152]

The combination presentation of base resin, a curing catalyst, etc. and the physical-properties evaluation result of the hardened material obtained from it are shown in Table 3.

101101

[Table 3]  
[Table 3]

condensation catalyst was measured, and also as a (C) ingredient, lauryl amine was used together with the above-mentioned base resin, the spatula was used by working example 16-28 and the comparative example 4 for it, and it stirred and mixed for 3 minutes to it, it was recuperated at 23 °C after mixing, and the surface hardened state was evaluated five days afterward. It was made for all the numbers of mols of the metal atom containing the number of addition parts of the various hydroxide alkali salt of the (B) ingredient to become the same here.

The evaluation result of the hardened state five days after the combination presentation of base resin, a curing catalyst, etc., is shown in Table 4. What the surface had hardened O in front for five days afterward is shown, and it is shown that x had not hardened five days after.

[illegible]

- [illegible]

1. <http://www4.indinitt.ro.jp/cgi-bin/transaction.cgi?u=http%3A%2F%2Fwww4.ipdl.i>

[illegible]

- [illegible]

When the various carboxylic acid metal salt of working example 6-15 is used compared with the comparative example 3 using 2-ethylhexanoic acid tin as a silanol condensation catalyst as shown in Table 3, the value of T<sub>b</sub> (breaking strength) and E<sub>b</sub> (elongation after fracture) of hardened material physical properties is larger.

Working example 16-28. comparative example 4)

(A) Using the mixture (A-2) of the isobutylene system polymer and plasticizer which have as an ingredient the reactive silicon group obtained in the synthetic example 2, various additive agents were measured, respectively, and it often kneaded with a 3 part roll according to the formula shown in Table 4, and was considered as base resin.

Next the various carboxylic acid metal salt shown in Table 4 as a (B) ingredient which is a silano-

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working example 29 and 31) which has a methyl dimethoxy silyl group.

[0192]

The same hardenability constituent as working example 6-15 can be prepared using the polyoxymethylene series polymer (A-3) which has the trimethoxysilyl group obtained in the synthetic example 3. The tack free time of this constituent has short cure time, and good physical properties are acquired.

(Constituent which used the epoxy resin together)

The same hardenability constituent as working example 6-15 can be prepared using the constituent which used together reactive silicon group containing organic polymer and an epoxy resin. When this constituent is used, the manifestation of adhesive strength is quick.

[0193]

[Effect of the Invention]

(A) The organic polymer which has the hydroxyl group or hydrolytic basis combined with the silicon atom, and has at least one silicon content group which can conduct a silyl by forming a siloxane bond, (B) Carboxylic acid calcium, carboxylic acid sodium, carboxylic acid potassium, carboxylic acid titanium, carboxylic acid cobalt, carboxylic acid barium. The hardenability constituent containing one or more carboxylic acid salts and metal salt which it comes to choose out of carboxylic acid magnesium, carboxylic acid nickel, carboxylic acid cobalt, and a carboxylic acid zirconium. While making practical hardenability and stability, the hardened material obtained shows the outstanding mechanical physical property which has high intensity and high elongation as compared with the case where the carboxylic acid tin currently used conventionally is used as a curing catalyst. Therefore, the hardenability constituent of this invention is very useful as various elastomers, such as a sealing material, adhesives, a binder.

[Translation done.]